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PRODUCTION AND PROPERTIES OF SEMI-FINISHED
TANTALUM

By Jeri Vacek

- GERMANY -

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PRODUCTION AND PROPERTIES OF SEMI-FINISHED TANTALUM

Following is the translation of an article by Jiri Vacek of the Research Institute for Powder Metallurgy, Vestec/Prague, in the German-language review Neue Huette (New Foundry), Vol. 2, No. 11, Leipzig, November 1957, pages 692-702.

Tantalum, a highly fusible metal of group V of the Periodic Table, is an invaluable material in modern chemistry, electrotechnics, vacuum techniques and many others because of its chemical, physical and technological characteristics. Ductile tantalum was first produced by W. v. Bolton [1] by smelting of a small compacted block of pure powdered tantalum obtained by reduction of potassium fluotantalate with sodium, in an electric-arc crucible under vacuum.

Due to the high cost by reason of the difficult method of production and the small amounts, semi-finished tantalum was utilized only very reluctantly. However, increased production of a suitable powdered tantalum, introduction of powder-metallurgical techniques and better knowledge of the properties of tantalum have aided in its wider distribution. By 1955, production of tantalum was almost thirteen times as high as in 1939 [2]. Industrially, semi-finished tantalum products are manufactured by sintering bars of compacted powdered tantalum under high vacuum [2-6]. Other production methods of the compacted metal are also known.

W. G. Burgers and J. C. M. Basart [7] have prepared ductile tantalum in wire form through thermic decomposition of tantalum pentachloride, supersublimated under vacuum, on a tantalum thread heated to 2,000° C under continuous vacuum in the apparatus. The authors obtained a deposition wire with a diameter of 1.25 mm within five hours. The wire was highly ductile and could be drawn out into threads of 25-50 u, without annealing.

H. A. Hohansen and J. A. May [8] reduced tantalum pentachloride with magnesium at 750° C. They removed the impurities from crude spongy tantalum by distillation at 900° at 10⁻³ Torr within four hours. The refined sponge was smelted down in the electric-arc with a tungsten electrode in an argon and helium atmosphere. Reduction gave a yield of 77.5%. The small tantalum block possessed a hard surface layer and a soft core (HRC = 33). The material was suitable for cold rolling with a 10% reduction per pass and a total pass reduction of about 93%. H. v. Zeppelin [9] had also reduced tantalum pentachloride with magnesium in the presence of potassium chloride and in a closed steel Carius tube more than ten years earlier.

Tantalum can also be prepared by reduction of tantalum pentachloride with hydrogen [10]. This process is used for tantalum coating of other metals [2] but not for production of the metal for further processing.

The utilization of tantalum is based on its physical and chemical properties. High melting point, low vapor point and electron-work function, together with good mechanical properties and primarily the ability for gas absorption (Getter), make tantalum invaluable in vacuum techniques. The specific electric properties of the oxide film formed by anodic oxidation of tantalum are utilized in electrotechnics. In the chemical and pharmaceutical industry as well as in medicine, tantalum is a preferred material by reason of its high resistance to many different reagents, good conductivity of heat, and low thermal expansion.

Tantalum is utilized for the production of electron tubes for very short waves, in current-impulse technics, for x-ray tubes at very high tension, current rectifiers and small electrolytic condensers. It is also used for spinning nozzles, for various refrigerating, heating, and secondary steam installation for aggressive media. Reaction tanks or agitators are coated with tantalum. In surgery, tantalum is used as a bone substitute as well as for surgical thread, needles and instruments. More details on the utilization of tantalum, including compounds of the latter, will be found in literature [3, 4, 11-15].

1 - Own Experiments. We investigated the compaction of powdered tantalum into small bars, the sintering of the latter under high vacuum, and the forming of the sintered bars into sheets, bars and wire. For sintering, vacuum-sintering bells were developed (one laboratory bell and one full-scale bell) and a molybdenum vacuum furnace for annealing.

Table 1 - Chemical Analysis of 3 Grades of Tantalum Powder in %.

Impurities	Grade			Impurities	Grade		
	I	II	III		I	II	III
Nb	2.84	1.08	0.62	Pb	-	-	0.001
Mg		0.011	0.003	K	0.0027	not determined	
Ca		0.007	0.004	S	0.169	not determined	
Cu	0.005	0.008	0.004	C	0.22	0.16	0.12
Ti	0.11	0.042	0.0065	O ₂	0.317	0.25	0.37
Si	0.008	0.009	0.056	N ₂	0.41	0.055	0.030
Fe	0.009	0.018	0.0095	H ₂	0.175	0.15	0.10
Al	-	0.0104	0.008				

The production of powdered tantalum which is obtained generally through reduction of potassium fluotantalate with sodium or potassium or through electrolysis of the given molten salt, was not undertaken. The experiments were carried out with powdered tantalum with a loose volume of 37 and a settled volume of 20.5 cm³/100g. Determined by the Blaine method /16/, its specific surface amounted to 2,510 cm²/g. The powder was screened with a mesh-width of 0.075 mm without residue. The other two grades of powder had similar characteristics and differed only somewhat in regard to content of impurities (Table 1).

1.1 - Compaction of Powdered Tantalum: In the experiments, the volume weight, the specific electric resistance, the necessary mass were determined in dependence on the compacting pressure in order to be able to compact bars of 5 x 5 x 100 mm³. We know that pure powdered tantalum can be compacted relatively well. The compacting pressures (4-12 ton/cm²) guaranty adequate density of the compacted shapes so that we can eliminate pre-sintering. This obviously reduces production costs because pre-sintering also takes place under vacuum. Moreover, the high pressure of compaction also increases the weight of the bars. This means a higher weight in comparison to the semi-finished products which are produced from a sintered bar.

During the experiments, we noted that the volume required for compaction is almost twice as great when we use a pressure of 14 instead of 2 ton/cm² (Fig. 1). The bars were compacted in a two-part press of which the bottom was stationary and the pressure was applied to the ram. As shown in Fig. 2, the volume weight of the compacted bars increases with increasing pressure of compaction. Simultaneously, their electrical resistance becomes reduced as will be seen from Fig. 3. Bars compacted at pressures of more than 3 ton/cm² and not pre-sintered, could be inserted in the clamps of the sintering bell without damaging their ends.

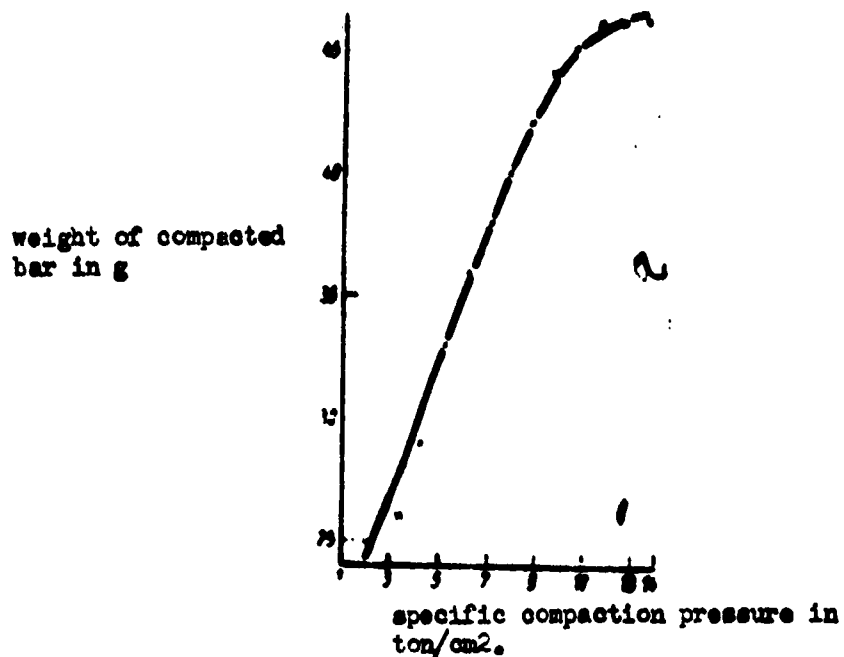


Figure 1 - Weights of Tantalum Powder for Different Compaction Pressures (5 x 5 x 100 mm³).

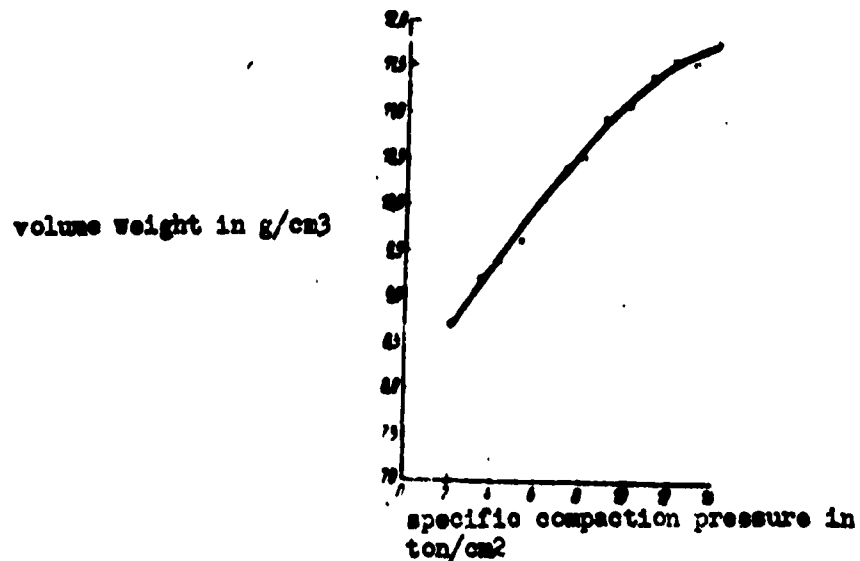


Figure 2 - Influence of Specific Compaction Pressure on Volume Weight of Compacted Bars.

specific electric resistance
in Ohm/cm²/m

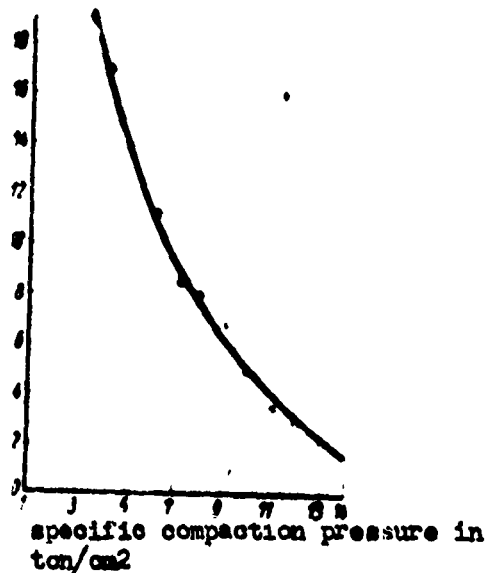


Figure 3 - Dependence on Compaction Pressure of Specific Electric Resistance of Compacted Bars.

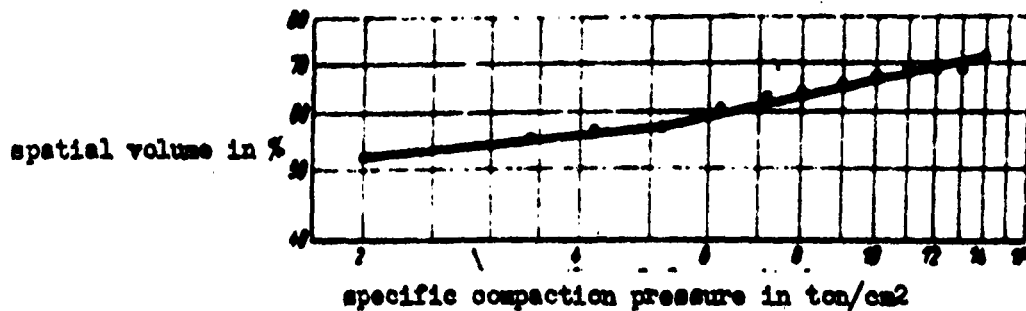


Figure 4 - Relation of Compaction Pressure and Spatial Volume of Compacted Bars.

If we calculate the ratio of volume weight of the formed bars to the spatial volume and enter the latter, in dependence on the pressure of compaction, in a double-logarithmic grid (Fig. 4), we see that the pressure equation of C. Agte and M. Peterdlik (17) is applicable to tantalum over a wide range of pressure. We may judge by the break in the curve that the ratio between plastic and elastic deformation changes in favor of plastic deformation at pressures over 5 ton/cm². The slope of the two parts of the curve indicates that the powder is not soft.

1.2 - Sintering: One of the most important processes in the production of semi-finished tantalum products by powder-metallurgical methods is the sintering of the compacted bars. Sintering of the bars is intended to give them not only a high volume rate and high density through optimum fusion of the individual grains but should also remove impurities, especially gases, from the sintered bars through the action of the high temperature. Optimum removal of gas from tantalum can be obtained only under high vacuum. Vacuum in sintering has two purposes: it protects the material against the action of practically all the gases with which tantalum reacts or which it absorbs at moderate to high temperatures. The vacuum must further contribute to the removal of gases already contained in the powdered substance or created by reaction among the existing impurities. When necessary, the vacuum must make possible the vaporisation of substances with a lower melting point (and/or with higher vapor pressure) than tantalum. It is therefore indicated to work with a dynamic vacuum, i.e. to constantly exhaust the equipment by pumping because, under static vacuum, the gases expelled may again be absorbed by the sintered bar after cooling. Moreover, the vacuum would become lower and lower in the course of temperature increase so that the removal of the gases which is possible only at high temperatures, might take place only under difficulties or perhaps not at all (cf. below).

Such rare gases as argon and helium carefully freed of other gases and vapors could be used as protective atmosphere. They are absorbed by tantalum only very little and their presence causes only minor changes in the properties of the metal. Their purification is complicated, however, and would bring about a further increase of the high costs inherent in their utilisation. When we consider the mean free distance of path of the gas molecules as a function of atmospheric pressure, it also becomes clear that, when utilising rare gases as protective atmosphere, the removal of gas from tantalum would take place very much slower which would mean again an increase of cost due to the longer duration of sintering.

1.21 - Sintering Installation: We first constructed a laboratory vacuum bell for sintering of tantalum (Fig. 5). The installation consists of the actual bell, the vacuum pump, the measuring instruments, and the electric current source. (Only part of the transformers can be seen at both sides of the picture). The actual sintering bell (Fig. 6) consists of welded steel plate with a water jacket and is provided with a visual aperture to which the measuring pipe of a vacuum meter is connected. The bell rests on a silver-coated steel plate which conducts current to the lower electrode. The upper electrode passes through the base plate, is isolated from the latter, and cooled with water. The lower electrode is cooled by radiation with the aid of radiation plates, is mobile, and counterweighted (Fig. 7). An opening (Fig. 7-a) is in the base plate for connecting the vacuum pump. A vapor condenser has been placed in the opening in Fig. 7-b.

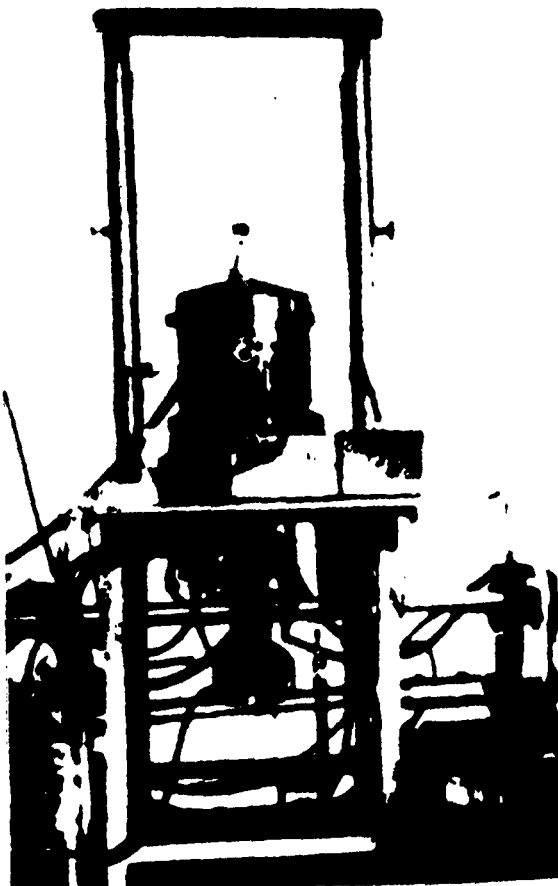


Fig. 5 - Laboratory Installation for High-Vacuum Sintering.



Fig. 6 - Vacuum Sintering
bell

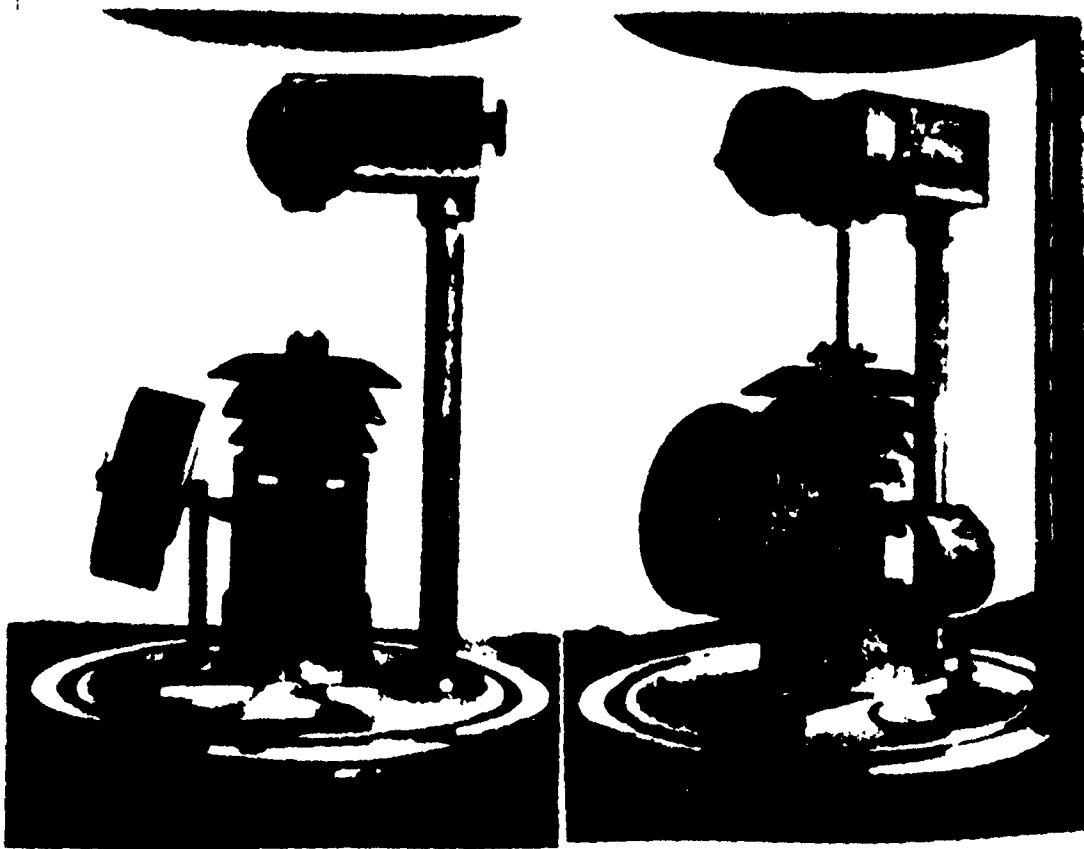


Fig. 7 a - Electrodes in
sintering Bell

Fig. 7 b - the same with bar
inserted

The pump consist of a single-stage rotary vacuum pump with a capacity of 15 m³/hr and a three-stage oil-diffusion vacuum pump with a capacity of 150 lit/sec.

1.22 - Measurement of Vacuum: For measurement of vacuum in the sintered bell, we used a thermoelectric vacuum meter of the type described by P. Hix and A. Lenk [18]. The millivoltmeter combined with it has a high internal resistance, the current was carefully stabilized and the heating current for the filament of the measuring tube changed. This enlarged the range of measurement of the vacuum meter for higher

and lower pressures. In addition to a larger range of measurement, this vacuum meter has the advantage of continuous measurement of vacuum.

The vacuum meter is calibrated for air by comparison to the indications of the abbreviated McLeod mercury vacuum meter. The result is shown graphically in Figure 8. In calibrating the curve B, a U-tube was connected between the thermoelectric vacuum meter and the bell. The walls of the tube were sprayed with phosphorous oxide supersublimated under vacuum. The tube was cooled from the exterior by a mixture of four parts of nitric acid, five parts of ammonium nitrate and eight parts of sodium sulphate. The temperature of the mixture varied between -31 to -35°C . McLeod's vacuum meter was connected directly to the bell and measures only the pressure of the permanent gases. However, the vapors of such liquids as water and oil condense in a compression capillary so that they escape measurement. The bell was pumped out for two hours. The pump was then stopped, atmospheric air was gradually admitted into the system and the pressure in the system measured.

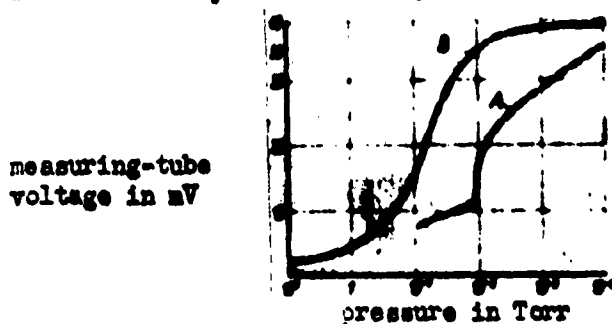


Figure 8 - Dependence of Measuring-Tube Tension of Thermoelectric Vacuum Meter

After termination of the experiment, the U-tube was removed, the bell left open for ten minutes, closed again and the vacuum measured during pumping. The curve A from the values obtained indicates the extent to which the McLeod vacuum meter distorts the value of the true vacuum. The space between the two curves corresponds to the pressure of the water vapor.

1.23 - Measurement of Temperature: When centering a highly fusible metal such as tantalum, temperature cannot be measured with a thermoelement but a pyrometer with decreasing filament must be utilized.

Consequently, reading of the true temperature is difficult. The visual aperture becomes coated with a thin film of the metal, reducing optical transparency and distorting the indications of the pyrometer. Moreover, the reflection of the tantalum surface changes during centering. For better understanding of the explanations below, we have given an explanation for some characteristics of temperature:

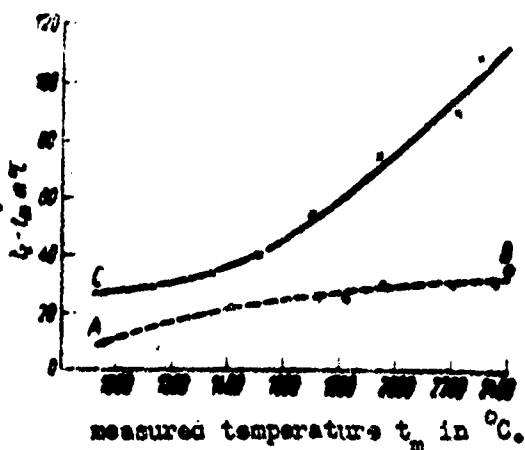
t_s = actual temperature of the surface of the tantalum ($^{\circ}\text{C}$);

t_z = apparent temperature which would be measured by the optical pyrometer if no light-absorbing medium existed between pyrometer and tantalum bar ($^{\circ}\text{C}$)

t_m = temperature measured by the pyrometer after light absorption through the visual aperture.

The absorption of radiation through the visual aperture was determined by inserting a similar analogous glass between the pyrometer and the visual aperture at different temperatures. For given temperatures of t_m , we thus obtained correction values corresponding to absorption radiation of the visual aperture. By adding these values, we can calculate the apparent temperature t_z . The relation observed is represented in Fig. 9 (curve A). The bar was maintained at $2,400^{\circ}\text{C}$ for ten minutes. After cooling, a clean glass was inserted and the bar brought again to $2,400^{\circ}\text{C}$. The temperature was measured both only with the clean glass in the visual aperture as well as with the one previously utilized (ten minutes at $2,400^{\circ}\text{C}$) which was inserted between the pyrometer and the clean glass. The correction value was slightly higher, due to a slight soot covering of the glass inserted (point B in Fig. 9).

Figure 9 - Correction of Pyrometer Indications for Observation Glass Utilized.



Apparently absorption increase due to the radiation on the visual aperture at a sintering duration to end temperature because the glass will become covered by an increasingly thicker covering of impurities. This could be demonstrated. The bar has melted after 90 minutes if it was kept at the temperature of 2,400°C as measured by the pyrometer. The temperature measurement became lower, however, due to the greater absorption of the radiation. The current was consequently increased and the bar melted although the measured temperature amounted presumably to 2,400°C. In all experiments, we therefore controlled the temperature with the pyrometer and maintained it at the selected temperature according to the current. The corrections were determined with the glass which indicated 2,400°C in the visual aperture for 240 minutes when heating the tantalum bar. After replacing this glass in the visual aperture by a clean glass, it was inserted between the pyrometer and the clean glass at given measured temperatures (t_m) when heating the tantalum bar. The dependence obtained is represented by curve C in Fig. 9. It will be noted that absorption by the contaminated glass is almost four times greater at $t_m = 2,400^\circ \text{C}$.

Some of the tantalum bars were melted. At the moment of melting, we can determine the difference between the actual and the apparent temperature, if we know the melting point exactly. The mean value of the apparent temperature was 2,638°C. From the equation

$$\frac{1}{T_1} - \frac{1}{T_2} = \frac{\lambda \log E_\lambda}{c_2 \log e}$$

in which T_1 = actual melting point of tantalum, 3,273°K; T_2 = apparent melting point of tantalum, 2,911°K; E_λ = partial radiation ability at wave length λ ; c_2 = constant of the Wien law, 14,350/u°K, the partial radiation ability $E_\lambda = 0.556$ was calculated on the assumption of constancy ($\lambda = \text{const.} = 0.65/\mu$) of the wave length indicating the maximum permeability of the red filter of the optical pyrometer. For this partial radiation ability, values of the actual temperature in the range of 2,300-2,700°C of the apparent temperature were calculated on the assumption that the partial radiation ability is constant within this range. The difference of the two temperatures

in dependence on apparent temperature is represented graphically in Figure 10. This linear dependence is that much more accurate, the closer the temperature is to the melting point.

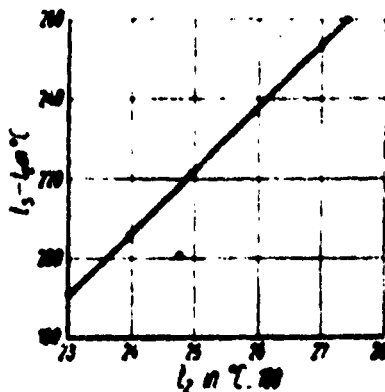


Figure 10 - Relation of True Temperature t_s to Apparent Temperature t_a
(tantalum, partial radiation capability $E \lambda = 0.556 = \text{const.}$)

1.24 - Influence of Sintering Temperature: For the sintering experiments, we utilized bars of 5 x 5 x 100 mm³ compacted at pressures of 6 and 12 ton/cm². The compacted bars were not presintered. In the first experimental series, a new compacted bar was used for each selected temperature. In the second experimental series, the bar was sintered in stages. It was first brought to the lowest selected temperature, permitted to cool, removed from the bar, and its values measured. The bar was then again inserted in the bell and brought to the next highest selected temperature and the procedure continued until reaching the highest selected temperature. No difference was determined between the two experimental series. The temperature was increased as a function of the vacuum, i.e. only after the vacuum meter indicated the selected value. At selected temperatures, the bar was always heated 5 minutes.

The volume weight, the linear shrinkage (length), the hardness HV₁₀, and the specific electric resistance were measured on the sintered bars. The results are graphically represented in Figure 11 for bars compacted at 6 ton/cm² and in Fig. 12 for bars compacted at 12 ton/cm². Practically, there was no difference between the bars.

According to the findings, the volume weight (after a slight drop initially) increases with increasing sintering temperature, linear loss also increases and specific electric resistance drops. The trace of the curve is customary in powder metallurgy for the indicated relations and entirely comprehensible. The dependence of hardness on sintering temperature is less clear because hardness reaches a maximum in the range of the measured temperatures from 1800-2,200° C. This dependence obviously is related closely to the fact that tantalum has the highest absorption of gas (Getter) at temperatures of about 1800° C and loses the absorbed gases only above 2,200° C [20]

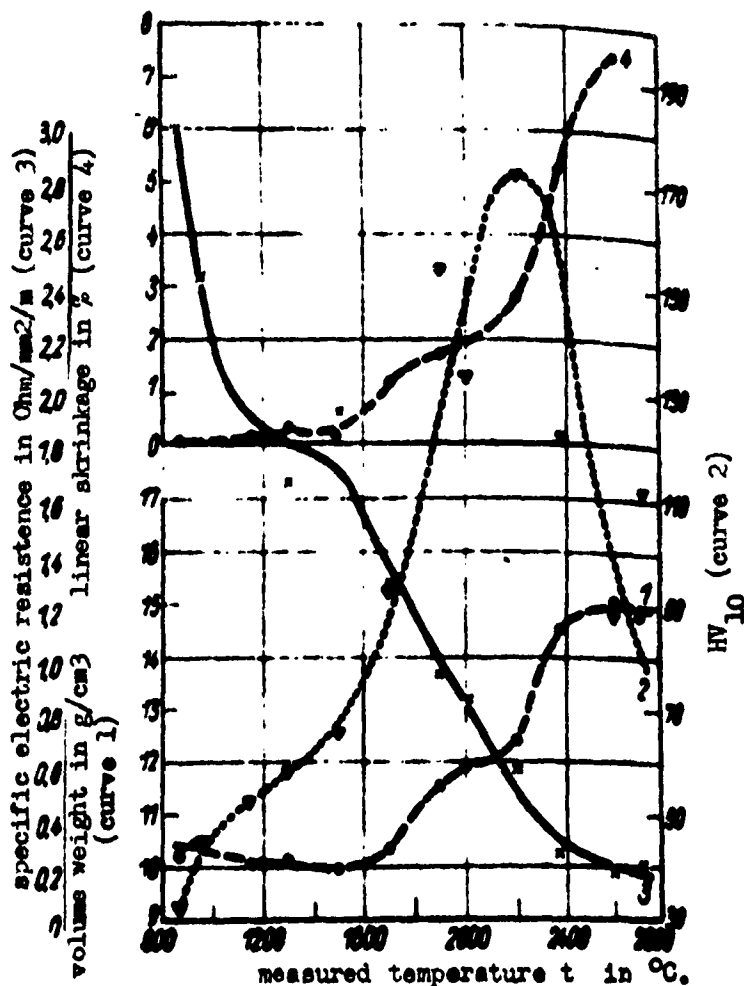


Figure 11 - Sintering of bars compacted with 6 ton/cm² at different temperatures.

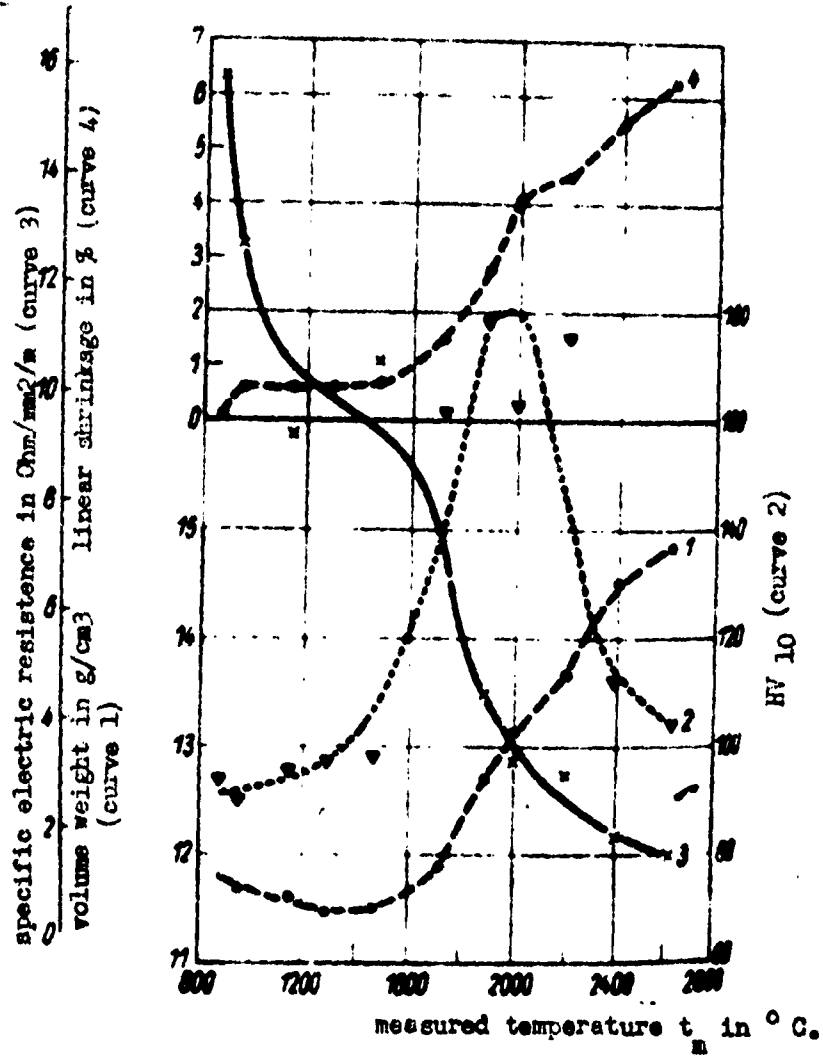


Figure 12 - Sintering of bars compacted with 12 ton/cm² at different temperatures

The trace of all curves agrees with the observations of Mamula and the author [19] according to which hydrogen is expelled in the range from 600-1200°C, carbon monoxide from 1,700-2,000°C, and nitrogen from 1,900-2,400°C.

By sintering a bar in stages, it was possible to determine the weight loss created by vaporization or expulsion of the substances from the bar during sintering. The findings for bars compacted under pressures of 6 and 12 tons/cm² from powdered tantalum I are represented graphically in Figure 13 which indicates that the losses rapidly increase above 1,700°C. These relatively high losses cannot be caused by the vaporization of impurities. In that case, the losses would amount to about 2.48% which corresponds to the total volume of impurities including columbium, decreased by the volume of impurities including niobium remaining in the sintered bar (cf. Table 1 and 3). Nor can such high losses of weight occur even we include also the vaporization of the tantalum, in addition to the vaporization of the impurities. According to calculation, [21] the vaporized volume should be 0.0087 g within 5 minutes when vaporization is not interfered with and the pressure of the tantalum vapors amounts to 10⁻⁴ Torr and 2,600°C; and should be about 10 times greater at 2,800°C. Because the losses mount up to 9 %, the cause must be sought in the fact that the fine particles of tantalum are entrained by the expelled impurities or, possibly, that tantalum becomes lost in the form of compounds.

It is reasonable to assume entrainment of the particles of tantalum because the sintered bars have a rough surface on the one hand and the losses are smaller in bars compacted under higher pressure on the other hand and also because the deposition in the bell contains predominantly tantalum (Table 2).

1.25 - Influence of Duration of Sintering: For these experiments, the bars were again compacted at 6 and 12 tons/cm². By sintering to terminal temperature selected as 2,400°C on the basis of the preceding experiments, the bars were maintained 5-120 minutes at this temperature. After sintering, we determined the values of the same characteristics as in the preceding experiments. The results are represented graphically in Fig. 14 and 15. The findings show that the specific electric resistance drops initially under continuous exposure, but remains practically constant after 45 minutes. The case is analogous for hardness. However, under long continued exposure to terminal temperature, volume weight and linear loss increase slightly. After 45 minutes, the values again remain practically constant.

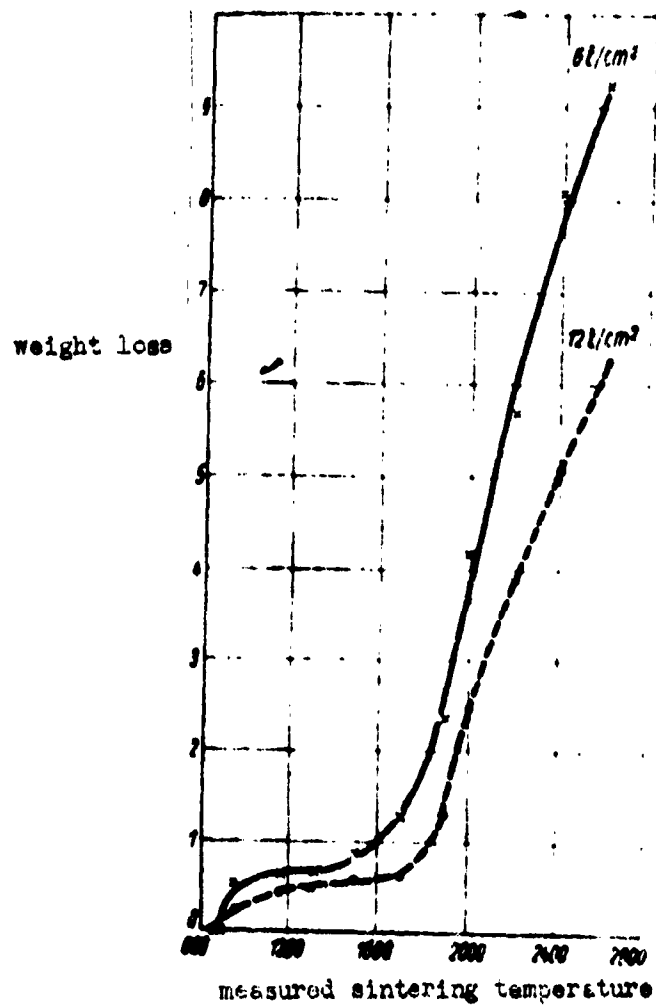


Figure 13 - Weight loss of sintered bars in relation to measured sintering temperature.

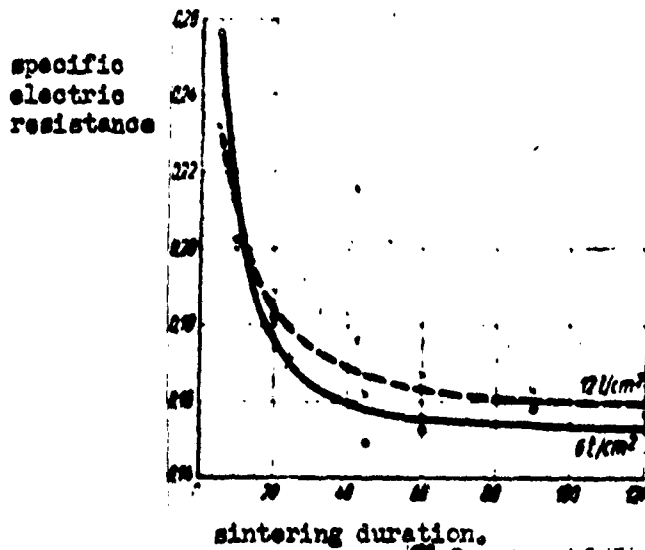


Figure 14 - Influence of sintering duration at 2,400°C on specific electric resistance of sintered bars.

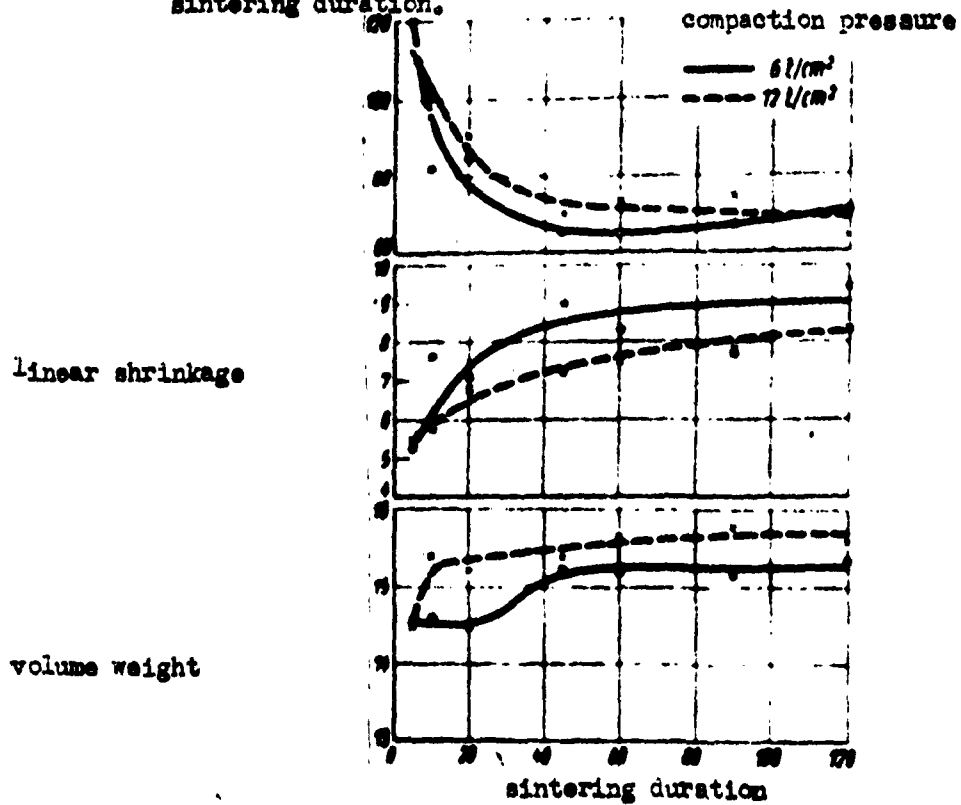
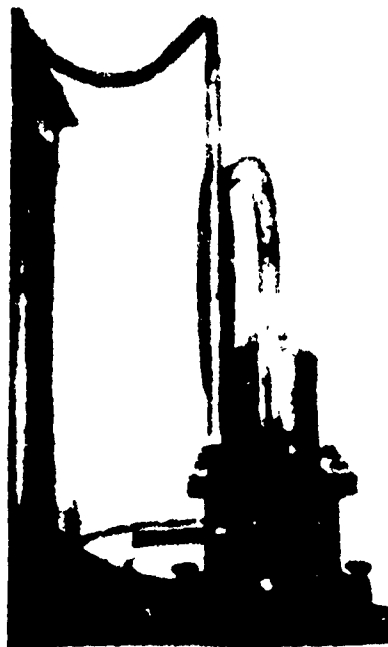


Figure 15 - Influence of sintering duration at 2,400°C on some properties of sintered bars.

All sintered bars were hammered into rods of 1.1 mm in diameter in the cold state, without intermediate annealing. They were easy to forge, had no cracks and were ductile. Contrary to indications in literature (e.g. 5), the sintering duration to terminal temperature was much shorter.

1.16: Spectron analysis of exhaust gases: In the construction of the sintered installation, we utilized a discharge tube with polydenum electrodes for the detection of leaks. Subsequently the discharge tube remained connected, during sintering, between the diffusion and the rotary vacuum pump (Fig. 16). It was shown that the color of discharge changes from pink to blue and later from blue to redish purple, depending on the type of gas. From a thermodynamic consideration confirmed experimentally through qualitative analysis of the exhausted gases, it appears that hydrogen, carbon monoxide and nitrogen were involved. A specially designed discharge tube was connected between the rotary and the diffusion vacuum pump. The spectra of the exhausted gases were photographed, at different temperatures of the sintered bar, by means of the spectrograph. Under analogous conditions, spectra of different pure gases and vapors were obtained. Comparison of the photos which were calibrated with mercury strokes, demonstrated qualitatively gases which are exhausted during sintering of tantalum.

Figure 16 - Discharge Tube



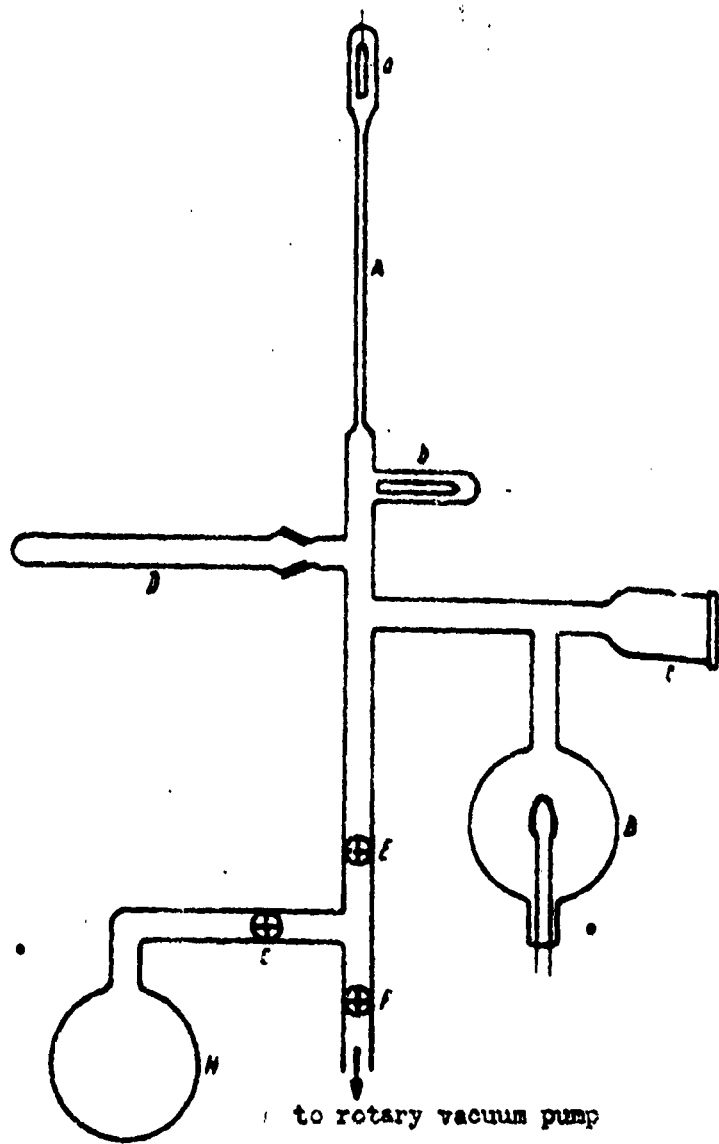


Figure 17 - Apparatus for Spectrum Analysis of Gases.

Figure 17 shows the diagram of an installation of glass consisting of a discharge tube A with molybdenum electrodes a and b, measuring tube of the thermoelectric vacuum meter C, the reaction retorts B, D, H and the stop-cocks E, F, G. The installation serves to produce pure gases from absolute reactions, for purposes of comparison. The gases drawn from the bell with the diffusion vacuum pump are dried and their pressure is regulated so that the spectra can be determined under analogous conditions. For these experiments, we utilized the "spektral-box" of the Fuess Company which also permits visual observation. With the aid of a lateral objective, the comparison spectrum of mercury was photographed (mercury lamp). It was experimentally confirmed that, during sintering of tantalum, hydrogen, carbon monoxide and nitrogen are dissolved in the following temperature ranges: Hydrogen, $t_g = 600-1,217^\circ\text{C}$; carbon monoxide, $t_g = 1,726-2,029^\circ\text{C}$; nitrogen, $t_g = 1,928-2,432^\circ\text{C}$. Detailed data on spectrum analysis of the exhausted gases will be found in [19].

1.27 - Increase of Temperature during Sintering: In order to determine optimum increase of temperature during sintering, experiments were carried out. In the first experimental series, temperature was increased in different intervals of time, e.g. by 100°C every ten minutes or every five minutes. In both cases, vacuum during sintering was adequate (5×10^{-4} Torr), i.e. the pump was capable of exhausting the gases at each stage. However, when increasing temperature by 100°C every 2.5 minutes, it was shown that the speed of increase was too high in the range from $1,700-1,200^\circ\text{C}$ and manifested itself by an inadequate vacuum (Fig. 18). In the range from $1,200-1,600^\circ\text{C}$, the speed of increase was too low on the other hand. This shows that it is not advantageous to increase the temperature uniformly in proportion to time.

If the temperature was raised after a previously determined vacuum (minimum 10^{-3} Torr), it was possible to accurately determine the end of degassing in the different sintering stages which were noted with the aid of spectrum analysis of the exhausted gases. This prevented us from obtaining unnecessarily low temperatures in the ranges in which degassing did not occur or was already terminated. The economic advantages of the method are apparent. It was shown further that it is not necessary to maintain a high vacuum (minimum 10^{-3} Torr) during the entire process of sintering. It is sufficient to exhaust the installation only with the rotary vacuum pump, to admit the current, and to begin simultaneously to warm up the diffusion vacuum pump. After dissolution of the moisture, primarily the

hydrogen, the vacuum drops. The greater part of the hydrogen is removed by the rotary vacuum pump and the remainder, at about 1,000°C, with the diffusion vacuum pump which has warmed up in the meantime. The vacuum then increases from 1×10^{-3} Torr to 5×10^{-4} Torr and must be maintained at that point until sintering is completed (Fig. 19). This method of sintering is a guaranty for economic operation and uniform characteristics of the bars.

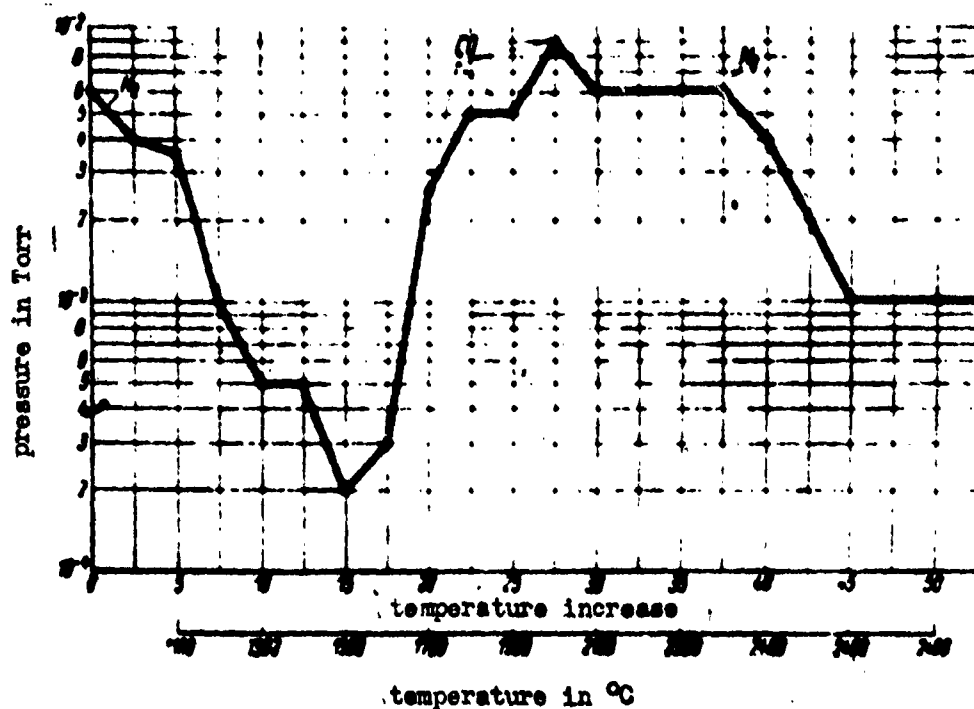


Figure 18 - Pressure change at uniform temperature increase (100°C/2.5 min).

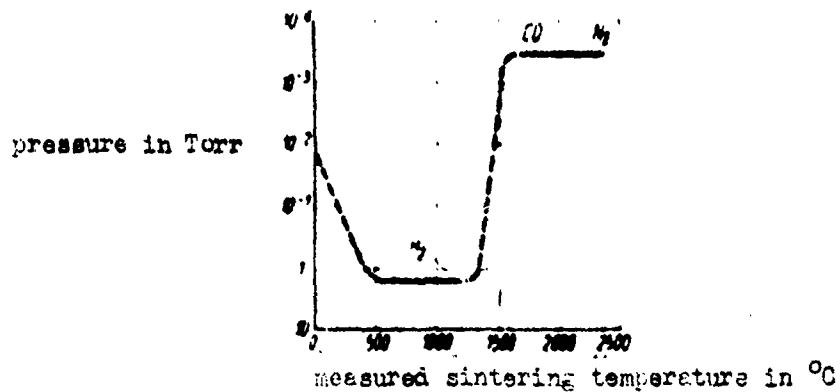


Figure 19 - temperature increase in relation to vacuum (Diagram)

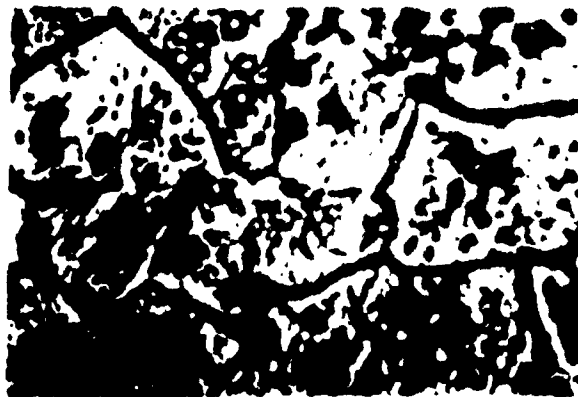


Figure 20 - Microstructure of sintered bar, etched HF/HNO₃, 200x.

The volume weight of the sintered bars per 100 bars lay between 15.0-15.2 g/cm³. specific electric resistance between 0.15 and 0.18 Ohm/mm²/m and hardness between 70-80 HV₁₀. The structure of a

sintered bar will be seen in Fig. 20. The lattice constant has a mean value of 3,299 Å / - 0.002 Å in limits from 3,294 to 3,304 Å

(CuK_α rays, reflection, 411). Without annealing, we rolled from the

sintered bars sheets of 0.10 mm including foil of 12/u and drew wire

of 0.15 mm. The chemical composition of such a sheet is shown in Table 3.

Table 3 - Chemical Composition of Tantalum Sheets.

<u>Impurity</u>	<u>%-wt</u>
columbium	1.79
oxygen	0.01
hydrogen	0.006
nitrogen	
silicium	0.0018
(sulphur	
copper, iron	-
titanium, alkali)	

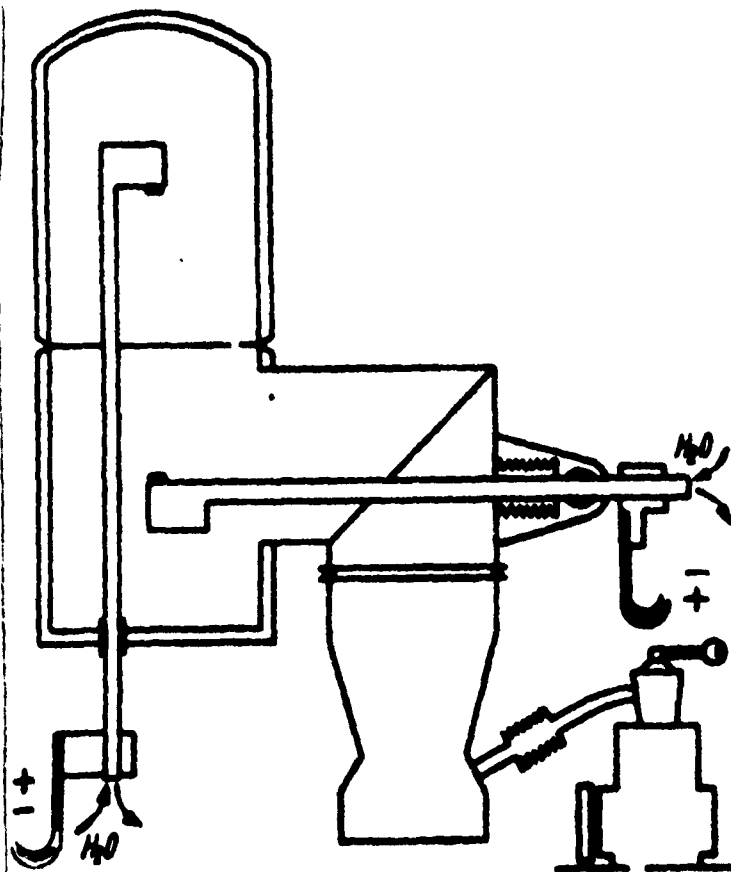


Figure 21 - Diagram of full-scale Vacuum Sintering Bell.

1.28 - Full-scale Vacuum Installation: On the basis of the experience gained, operational sintering bells were designed and a diagram of one of the latter is shown in Fig. 21. Here both electrodes are waterproof because otherwise the radiation panels and foil bundles utilized in laboratory equipment would form far too large a surface in the bell which would be unfavorable from the point of view of the vacuum. Furthermore, the dimensions of the bell would become too large. The lower electrode is designed as a horizontal lever, pivots around its axis and is arranged outside of the vacuum space. The lever is sealed against leakage by a flexible metal hose. Electric current is supplied by a bundle of copper foil. The electrode has an adjustable counterweight.

The bell itself is constructed of welded sheet aluminum and consists of two parts with water jackets. The upper part can be raised by means of an electric motor. It is provided with a tube and a quartz window which is protected against contamination by soot and against radiation by a metal mask which is operated from the exterior by a magnet. The exhaust line of the diffusion vacuum pump is welded to the lower part with a condenser connected in the line between bell and condenser. A tap for the measuring tube of the vacuum meter is also provided. The closure consists of a plate through which the upper electrode projects.

The pumping device consists of a four-stage diffusion vacuum pump with a capacity of 1,000 lit, a rotary vacuum pump with a capacity of 30 m³/h and a vacuum stop valve in the range of the low vacuum. The entire installation (except the top part of the bell) is enclosed in the same housing and all devices are operated from the exterior (fig. 22).

2 - Forming of Sintered Bars: When the sintered tantalum is adequately free of gas and impurities, it becomes ductile i.e. further processing poses no particular difficulties. To a certain extent, this compensates for the difficulties of sintering under high vacuum. On the basis of different characteristics, it is possible to judge the ductility of the metal after it has been sintered. If the specific electric resistance of 0.30 Ohm/mm²/m is exceeded, this is due either to unsatisfactory sintering or the presence of impurities. It is therefore necessary to determine the volume weight of the bar; if this exceeds 14.5 g/cm³ (Fig. 23), the high value of specific electric resistance is most probably caused by impurities. This can be checked by measurement of hardness which should not exceed 100 units HV₁₀ for satisfactorily malleable sintered bars.

of 0.15 mm. The chemical composition of such a sheet is shown in Table 3.

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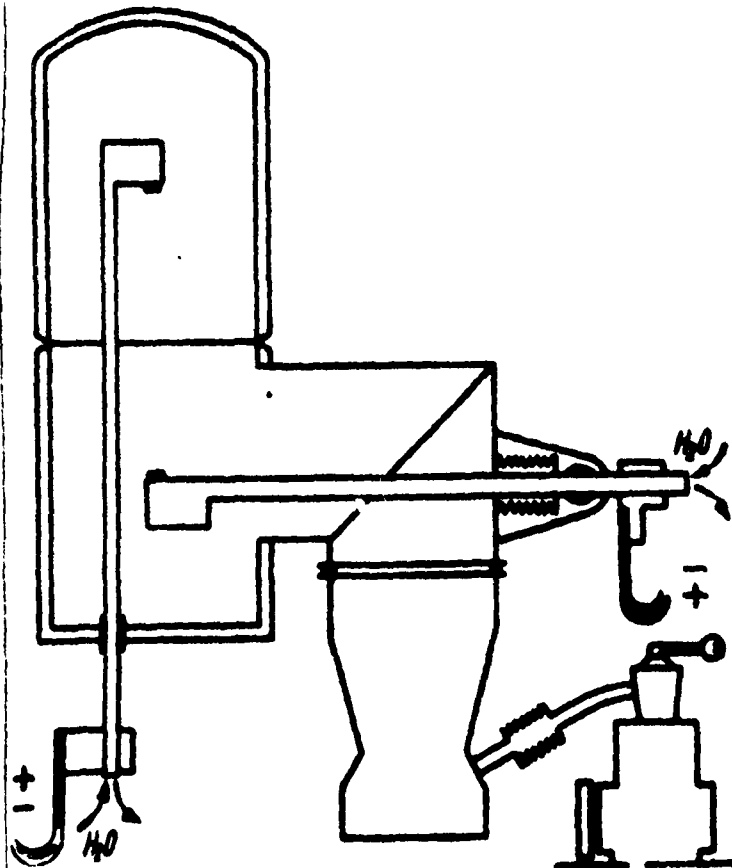


Figure 21 - Diagram of full-scale Vacuum Sintering Bell.



Figure 22 - Overall View of Operational Vacuum Sintering Bell.

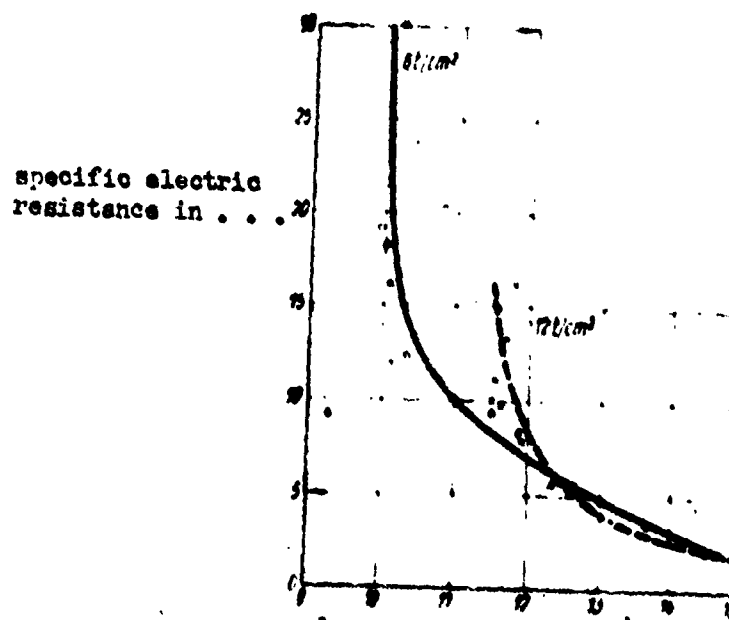


Figure 23 - Relation of Volume Weight to Specific Electric Resistance

All types of forming operations take place at normal temperature. As already mentioned, the sintered bars can be formed without annealing. However, it is customary in practice to carry out intermediate annealing, also designated as re-sintering because it is performed under the same conditions as sintering. Such re-sintering is advantageous because eventual residual gases are removed and because it saves wear and tear on the forming machines and/or the parts directly involved in forming. Forming operations pursue two purposes:

- a) to eliminate the remaining pores (about 10%) in the preliminary stages (together with re-sintering);
- b) to give the desired form to the material during the further stages of the forming operation.

For experimental production of sheets, the non-sintered ends were cut off; the bars were then formed into flat shapes and subsequently re-sintered for 30 minutes at $2,400^{\circ}\text{C}$ in a vacuum higher than 10^{-3} Torr. We experimented with flattening these sintered bars with a compressed-air hammer, in a power press, or in a rolling mill.

Forming with the compressed-air hammer is the least advantageous because the material receives uneven edges which must be cut off, thus causing increased waste. Forming of the bars in a hydraulic press is more advantageous because the bars are formed with perfectly straight edges, only a little narrower at the ends. Since they cannot be formed to the original length because the non-sintered ends were removed, it is necessary to change the electrode gap during re-sintering and to utilize high specific pressures (about 20 ton/cm² for a degree of forming of 40-50%). The bar can also be rolled; the edges are straight up to the ends and with the pass reduction of 45 to 50%, we again obtain the original length for the flat bar. However, in this case the width (enlargement) is low. It is therefore advantageous to stamp flat bars for sheets.

Through forming, volume weight, hardness, and specific electric resistance increase proportional to the degree of forming. Annealing further increases volume weight but hardness and specific electric resistance drop. The degree of forming has no basic influence on the quality of the sintered bars nor on the quality of the sheets produced from them in which only the tensile strength is somewhat increased with increasing degree of forming.

The annealed and flattened bars were cold-rolled with a decrease in height per pass of 4-3%, depending on the width of the

material and the rolling equipment utilized. The amount of pass reduction can be selected in proportion to width of the material, even in a low-powered rolling installation. During rolling, the sheets are lubricated with light mineral oil but thin sheets and sheets during the final pass are lubricated with linseed oil. Narrow bands from wires or forged rods are advantageous for rolling because the edges become perfectly smooth.

For the experimental production of wire, the non-sintered ends were removed and the bars were forged into rods in the cold state. The decrease in cross-section, related to one hammer jaw, was up to 48% during the experiments but it was then difficult to feed the bar to be forged into the hammering machine. We therefore used graduated jaws so that a decrease of cross section, related to one jaw, of 16-20% resulted for an average hammering machine and of 20-30% for a continuous (small) hammering machine. The hammered bars were annealed at a total decrease of cross section of about 40% as described above. Generally of a diameter of 1.5 mm, the hammered bars were then drawn out to a diameter of 0.02 mm in metal dies or to a diameter of 0.150 mm with diamond dies, without re-sintering. Decrease of cross section in one draw amounted to about 11.5% with metal dies and 6% with diamond dies.

Wire drawing is much more difficult than rolling of sheets. Tantalum easily adheres to the drawing dies and is difficult to lubricate. Because of the very minor densification by drawing, the latter must be restricted to short stretches. In order to make the lubricant adhere to the tantalum wire, it is absolutely necessary to oxidize the wire surface. This can be done by a short interval of heating at 500-600°C in the air or preferably by anodic oxidation in 1% sulphuric acid or sodium-sulphate solution. The most suitable color of the oxide film is purple steel-blue. With thicker wires, it is advantageous to re-oxidize after each draw and, for thinner wire, after two or three draws. When using diamond dies, the residual oxide coating after drawing with metal dies is sufficient for nine diamond dies. Suitable lubricants are beeswax, an emulsion of tallow and soap, colloidal graphite (relatively unsuitable), or an emulsion of tallow and soap with the addition of colloidal graphite and turpentine. We tested all these lubricants and all were satisfactory, except colloidal graphite. Because the tests were carried out under semi-operational conditions, it was not yet possible to determine which of these lubricants best preserves the drawing dies.

3 - Waste Recovery: In the manufacture of semi-finished products, waste occurs. Since the latter is generally ductile, it cannot be

simply crushed and ground to powder and must first be made brittle. Tantalum is therefore exposed to hydrogen at increased temperature. Hydrogen dissolves in the tantalum and the latter becomes brittle and friable. Whether this produces tantalum hydride, has not yet been definitely determined.

For the hydrogenation of the tantalum waste, electrolytic hydrogen was purified in the customary manner and brought in contact with a titanium sponge heated to 800-850°C; it then entered the stove pipe (autoclave?) with the tantalum waste which had been heated to 450°C. The waste was cooled after 3 hours, removed from the autoclave, crushed and ground in a ball mill. The resulting powder was leached with hydrochloric acid to remove iron (from friction in the mill) and washed first with water and then with methyl alcohol. The washed powder was dried under vacuum at 60°C; it contained 0.3% hydrogen, and x-rays showed no other structural component. The lattice was very extensive and had a constant of $3,411 \text{ \AA} - 0.002 \text{ \AA}$.

The hydrogenated tantalum powder was mixed with fresh powder, compacted into bars sintered by standard procedure and processed into sheet or wire. The semi-finished products were excellent. Unless the mixture contained more than 50% of regenerated powder, no difficulties were encountered. However, difficulties already began when compacting the mixture with a higher percentage of regenerated powder. Wire produced from such a mixture cracked.

4 - Some Properties of Semi-Finished Tantalum Products: Experimentally observed properties had the following average values:

- a) Sintered Bars: Volume weight, 15.2 g/cm³; specific electric resistance, 0.181 Ohm/mm²/m; hardness, 82 HV₁₀; tensile strength, 55 kg/mm²; elongation to rupture, 1.7 %.
- b) Annealed and Forged Bars (Resintering): Volume weight, 16.55 g/cm³; specific electric resistance, 0.147 Ohm/mm²/m; tensile strength, 36 kg/mm²; elongation to rupture, 32 %.
- c) Forged and Non-Resintered Bars, Dia. 1.2 mm: Volume weight, 16.66 g/cm³; specific electric resistance, 0.155 Ohm/mm²/m; tensile strength, 78 kg/mm²; elongation to rupture, 2.4 %.
- d) Forged and Resintered Bars, Dia. 1.2 mm: Specific electric resistance, 0.140 Ohm/mm²/m; tensile strength, 38 kg/mm²; elongation to rupture, 12 %.
- e) Non-Annealed Sheets, 0.2 mm: (The samples were taken in the direction of rolling) specific electric resistance, 0.175 Ohm/mm²/m; tensile strength, 93 kg/mm²; elongation to rupture, 1.5 %; Erichsen (sheet-metal ductility) test, 1.13 mm.

The listing shows that the experimentally obtained values corresponds to those indicated in literature.

Conclusion: The possibilities for producing and utilizing parts of tantalum and a powder-metallurgical process are described in detail. The degree of compacting pressure for tantalum bars of finely divided tantalum metal powder has a high influence on the properties of the compacted bars. The latter are sintered under high vacuum by direct conduction of current without presintering. Detailed investigations concern the influence of sintering temperature and duration on the properties of the supersintered bars and their loss of weight and indicate different procedures for increasing sintering temperature. Measurement of temperature and of vacuum as well as spectrum analysis of the expelled gases are important. Experiments of forming supersintered bars by flat forging, pressing and rolling together with round-forging and drawing give an appreciation of finish-processing possibilities. Experiments with tantalum waste recovery are particularly significant. The properties of experimentally obtained products are given.

Summary: The report describes the author's experiments: compaction of powdered tantalum, sintering, sintering installation, vacuum measurement, temperature measurement, influence of sintering temperature and duration, spectrum analysis of exhaust gases, increase of temperature during sintering, full-scale vacuum installation, working of sintered bars, waste recovery; some properties of semi-finished tantalum products.

Literature References

- [1] v. Folten, E. : Z. f. Elektrochemie 11 (1905) H. 3, S. 45 bis 51.
- [2] Placek, Ch., and D. P. Taylor: Ind. Engng. Chem 48 (1956) S. 686 bis 695.
- [3] Balke, C. W. : Ind. Engng Chem 30 (1938) H. 3, S. 251 bis 254.
- [4] Miller, G. L. : The Industrial Chemist 295 (1949) H. S. S. 363 bis 390
- [5] Myers, E. H. : Metallurgia 38 (1948) S. 307 bis 310
- [6] Vacek, J. : Hutnickelisty 11 (1956) H. 9, S. 522 bis 529
- [7] Burgers, H. G., and J. C. W. Essart: Z. f. anorg. allg. Chem. 216 (1934) S. 223 bis 227
- [8] Johansen, H. A., and S. L. May: Ind. Engng. Chem. 46 (1954) H. 12 S. 2499 und 2500.
- [9] v. Zeppelin, H.: Metall und Ltz 40 (1945) S. 252
- [10] Powell, C. F., I. L. Campbell und E. W. Genser; J. Electrochem Soc 93 (1948) S. 258 bis 265

- 11 Espe, W.: Slaboproudy obsor 14 (1953) H. 5, S. 213 bis 223.
- 12 Rose, K.: Materials and Methods 26 (1947) H. 4, S 94 bis 98
- 13 Gayle, T. M.: Materials and Methods 39 (1954) H.1, S 94 und 95
- 14 Schofield, M.: Chem. Engng. 31 (1950) H. 3 S 111 and 113
- 15 Anonym; La Technique Moderne 43 (1951) H. 1 S. 18 bis 21
- 16 Gille, F.: Zement-Kalk-Gips 4 (1951) H. 4 S 84 bis 89
- 17 Agte, C., und M. Petrdlik: Hutnicke listy 7 (1952) H. 3 S. 121 bis 124
- 18 Hix, P., und R. Lenk: Slaboproudy obsor 14 (1953) H. 3, S. 128 bis 132.
- 19 Mamula, M., und J. Vacek; Hutnicke listy 11 (1956) H. 11, S. 654 bis 661.
- 20 Myers, R. H.: Metallurgia 41 (1950) S. 301 bis 304
- 21 Espe, W., und P. Hix: Slaboproudy obsor 15 (1954) H. 3, S. 18.

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